Contents

Preface xi

1 The ABX₃ Perovskite Structure 1
  1.1 Perovskites 1
  1.2 The Cubic Perovskite Structure: SrTiO₃ 4
  1.3 The Goldschmidt Tolerance Factor 6
  1.4 ABX₃ Perovskite Structure Variants 11
  1.5 Cation Displacement: BaTiO₃ as an Example 12
  1.6 Jahn–Teller Octahedral Distortion: KCuF₃ as an Example 16
  1.7 Octahedral Tilting 19
    1.7.1 Tilt Descriptions 19
    1.7.2 Trigonal Symmetry: LaAlO₃ as an Example 24
    1.7.3 Orthorhombic Symmetry: GdFeO₃ and CaTiO₃ as Examples 26
  1.8 Symmetry Relationships 30
  1.9 Hybrid Organic–Inorganic Perovskites 33
  1.10 Antiperovskites 34
    1.10.1 Cubic and Related Structures 34
    1.10.2 Other Structures 36
  1.11 Structure-Field Maps 36
  1.12 Theoretical Calculations 38
References 40
Further Reading 40

2 ABX₃–Related Structures 42
  2.1 Double Perovskites and Related Ordered Structures 42
    2.1.1 Rock-Salt Ordered Double Perovskites 42
    2.1.2 Other Ordered Perovskites 45
    2.1.3 AA'B₃O₁₂–Related Phases 48
2.2 Anion Substituted Perovskites 51
2.2.1 Nitrides and Oxynitrides 51
2.2.2 Oxyfluorides 53
2.3 A-Site-Deficient Perovskite Structures 54
2.3.1 ReO₃, WO₃ and Related Structures 54
2.3.2 Perovskite Tungsten Bronzes 55
2.3.3 A-Site-Deficient Titanates, Niobates and Tantalates 55
2.4 Anion-Deficient Phases Containing Tetrahedra 57
2.4.1 Brownmillerites 57
2.4.2 Brownmillerite Microstructures 62
2.4.3 Temperature Variation and Disorder 63
2.4.4 B-Site Doped Brownmillerite Phases 64
2.4.5 B-Site Doping and Oxygen Pressure 65
2.4.6 A-Site Doped Brownmillerite Phases 65
2.4.7 Brownmillerite-Related Phases 66
2.5 Anion-Deficient Phases Containing Square Pyramids 69
2.5.1 Manganites 69
2.5.2 SrFeO₂.₅ and Related Phases 71
2.5.3 Cobaltite-Related Phases 73
2.6 Point Defects, Microdomains and Modulated Phases 74
Further Reading 78

3 Hexagonal Perovskite-Related Structures 79
3.1 The BaNiO₃ Structure 79
3.2 BaNiO₃-Related Phases Containing Trigonal Prisms 81
3.2.1 Commensurate Structures 81
3.2.2 Modulated Structures 89
3.3 Perovskites with Mixed Hexagonal/Cubic Packing: Nomenclature 92
3.4 Perovskites with Mixed Hexagonal/Cubic Packing: Stacking Sequences 95
3.5 Hexagonal Perovskites with chq and c ph Stacking 98
3.5.1 (chq) Structures 98
3.5.2 (c ph) Structures 99
3.5.3 c ph Intergrowth Structures 104
3.6 Hexagonal Perovskites with c hh Stacking 106
3.6.1 (cc…chh) Aₙ B O₃ₙₙₚ Structures 107
3.6.2 (cc…chh) Aₙ B O₃ₙ₋₁ₚ Structures 108
3.6.3 (hhcc…chhcc…c) Intergrowth Phases 110
# Contents

## 6 Dielectric Properties 176

6.1 Insulating Perovskites 176
6.2 Dielectric Perovskites 178

### 6.2.1 General Properties 178
### 6.2.2 Colossal Dielectric Constant Materials 181
6.3 Ferroelectric/Piezoelectric Perovskites 182

### 6.3.1 Spontaneous Polarisation and Domains 182
### 6.3.2 Ferroelectric Domain Switching 185
### 6.3.3 Ferroelectric Hysteresis Loops 188
### 6.3.4 Temperature Dependence of Ferroelectricity 189
### 6.3.5 Pyroelectrics, Piezoelectrics and Crystal Symmetry 191
### 6.3.6 Strain versus Electric Field Loops 192
6.4 The Development of Ferroelectric/Piezoelectric Ceramic Bodies 193

### 6.4.1 Ceramic Piezoelectrics 193
### 6.4.2 Electrostriction 195
6.5 Antiferroelectrics 196
6.6 Ferrielectrics 199
6.7 Relaxor Ferroelectrics 200

### 6.7.1 Macoroscopic Characteristics of Relaxor Ferroelectrics 200
### 6.7.2 Microstructures of Relaxor Ferroelectrics 202
6.8 Improper Ferroelectricity 206
6.9 Doping and Modification of Properties 208
6.10 Nanoparticles and Thin Films 212
References 215
Further Reading 215

## 7 Magnetic Properties 217

7.1 Magnetism in Perovskites 217
7.2 Paramagnetic Perovskites 219
7.3 Antiferromagnetic Perovskites 222

### 7.3.1 Cubic Perovskite-Related Structures 222
### 7.3.2 Hexagonal Perovskites 229
7.4 Ferromagnetic Perovskites 233
7.5 Ferrimagnetic Perovskites 236
7.6 Spin Glass Behaviour 237
7.7 Canted Spins and Other Magnetic Ordering 238
7.8 Thin Films 240
7.9 Nanoparticles 243
8 Electronic Conductivity 247

8.1 Perovskite Band Structure: Metallic Perovskites 247

8.2 Metal–Insulator Transitions 250
  8.2.1 Titanates and Related Phases 250
  8.2.2 LnNiO₃ 252
  8.2.3 Lanthanoid Manganites 253
  8.2.4 Lanthanoid Cobaltites 254
  8.2.5 (Sr, Ca)₂RuO₄ and Ca₂Ru₁₋ₓCrₓO₄ 255
  8.2.6 NaOsO₃ 256

8.3 Perovskite Superconductors 257

8.4 Cuprate High-Temperature Superconductors 258
  8.4.1 Overview 258
  8.4.2 Lanthanum Cuprate, La₂CuO₄ 259
  8.4.3 Neodymium Cuprate, Nd₂CuO₄ 260
  8.4.4 Yttrium Barium Copper Oxide, YBa₂Cu₃O₇ 261
  8.4.5 Perovskite-Related Structures and Series 263
  8.4.6 The Generic Superconductivity Phase Diagram 263
  8.4.7 Defects and Conductivity 265

8.5 Spin Polarisation and Half-Metals 267

8.6 Charge Ordering and Orbital Ordering 268

8.7 Magnetoresistance 270
  8.7.1 Collosal Magnetoresistance (CMR) in Manganites 270
  8.7.2 Low-Field Magnetoresistance 272

8.8 Semiconductivity in Perovskites 272

8.9 Thin Films and Surface Conductivity 275

References 275
Further Reading 275

9 Thermal and Optical Properties 277

9.1 Thermal Expansion 277
  9.1.1 Normal Thermal Expansion 277
  9.1.2 Thermal Contraction 280
  9.1.3 Zero Thermal Expansion Materials 283

9.2 Thermoelectric Properties 284

9.3 The Magnetocaloric Effect 287
## Contents

9.4 The Pyroelectric and Electrocaloric Effect 288  
9.5 Transparency 289  
9.6 Electrophoric Films 291  
9.7 Electro-optic Properties 293  
  9.7.1 Refractive Index Changes 293  
  9.7.2 Electro-optic Phase Modulators 294  
  9.7.3 Electro-optic Intensity Modulators 296  
  9.7.4 Ceramic Modulators 299  
9.8 Perovskite Solar Cells 299  
Reference 302  
Further Reading 302

### Appendix A
The Bond Valence Model for Perovskites 303

### Appendix B
Summary of the Kröger–Vink Defect Notation 307

Index 309